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Short communication

Formation of three-dimensional honeycomb-like nitrogen-doped graphene for use in energy-storage devices

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ABSTRACT

We have developed a one-step method to produce three-dimensional honeycomb-like nitrogen-doped graphene. Interlaminated hybrid composites of phthalocyanine (Pc) and graphene oxide (GO) swell up when hydrogen is released from the layers during the solid-state pyrolysis process, producing the three-dimensional graphene. The unique micro-structural features of the honeycomb-like nitrogen-doped graphene possesses a high surface area of ~230 $m^2 g^{-1}$ and a substantial content of nitrogen (~4.03%). The planar-N configuration is found to significantly enhance the electrochemical property, due to the improved electrical conductivity and enhanced capacitance in KOH aqueous electrolyte in reversible Faradic redox reactions. The supercapacitor based on the honeycomb-like nitrogen-doped graphene presented outstanding specific capacitance (175 $F\cdot g^{-1}$ at 0.5 $A\cdot g^{-1}$) and a long cycle life of more than 5000 cycles. This work provides an opportunity for the mass production of 3D nitrogen-doped graphene for industrial application.

1. Introduction

Graphene and its derivatives are versatile building blocks for bottom-up assembly of advanced functional materials [1]. In particular, graphene has an exceptionally large specific surface area, excellent electrical conductivity, and superior chemical/electrochemical stability. This makes graphene the ideal material for various electrochemical energy storage devices including supercapacitors [2–5]. However, because of the strong π–π interaction between graphene sheets, graphene flakes tend to restack to form graphite-like powders when they are processed into practical electrode materials, which can greatly lower specific surface area and lead to inefficient use of graphene layers for electrochemical energy storage. The self-assembly of two-dimensional (2D) graphene sheets into three-dimensional (3D) frameworks can largely retain the unique properties of individual graphene sheets and has recently attracted interest for fundamental investigations and potential applications in diverse technologies [6,7]. The formation of 3D graphene networks can effectively prevent graphene from restacking and retain the high specific surface area that is necessary to achieve high specific capacitance. Additionally, because the highly interconnected graphene network facilitates electron transport and the interpenetrating porous network allows rapid ion transport, 3D graphene macrostructures are ideally suited for use as supercapacitor electrodes.

Nitrogen doping is a simple but useful process for graphene because it easily manipulates local electronic structure and can improve device performance in various applications including biosensors, fuel cells, and electronic devices. In particular, the manipulated local electronic structure obtained by nitrogen doping can enhance binding with ions in solution. This feature can be utilized for high-capacity energy storage devices; for example, high-capacity supercapacitors based on nitrogen-doped graphene have been reported. Nitrogen doping has also been shown to increase the capacitance of graphene EDLCs [4]. A summary of various methods used for the synthesis of N-graphene have been discussed in Table S1, most synthesis treatments may lead to surface doping by decorating the functional group of GO with suitable nitrogen source, thus the functional group becomes the key factor limiting the contents and bonding configurations. The calculation results of the specific capacitance reported in different works vary with the mass of the electrode in EDLCs and calculation method between two-electrode and three-electrode [8].

In this paper, we develop a simple, innovative and efficient strategy to produce 3D honeycomb-like nitrogen-doped graphene through solid-state pyrolysis, which compares favorably with complicated template-based methods [9,10], solvo-thermal method

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with special reaction condition in autoclave and expensive chemical vapor deposition [11–13]. Besides, we introduce the new nitrogen-graphene planar to assist the GO other than the major N-doping methods which focus on decorating the functional group of GO [14]. The production is obviously much higher than most methods we have mentioned before, and our further work has verified the production scale-up design, significantly, such 3D graphene contains abundant nitrogen component and exhibits outstanding electro-chemical behavior in terms of highly specific capacitance and excellent cyclability when used as electrode materials for supercapacitors, it's promising for industrial application.

2. Experimental section

2.1. Materials

The 3D graphene was prepared as follows: GO and metal-free Pc were synthesized according to reference [15] with minor modification. Pc (3 g) was added to a solution of GO in 200 mL sulfuric acid (1 mg mL^{-1}) and stirred for more than 24 h. The resulting GO-Pc mixture was isolated by centrifugation, washed with deionized water, and then vacuum dried at 60 °C for 24 h. The Pc-GO precursor was pyrolyzed in a quartz boat at 800 °C to obtain final 3D honeycomb-like nitrogen-doped graphene. The pyrolysis temperature and heating rate are the same as in our previous work [16]. For comparison, GO and Pc were pyrolyzed using the same procedure; the products are denoted as 2D reduced GO (2D graphene) and plate-like carbon (Pc carbon), respectively.

2.2. Characterization

The synthesized products were characterized by X-ray Diffraction (XRD) (Rigaku RINT 2400 with Cu Kα radiation), Scanning Electron Microscopy (SEM) (JSM, 6490LV) and Transmission Electron Microscopy (TEM) (Hitach, H600). UV–vis absorption spectra were recorded using a UV-2450 spectrophotometer. The specific surface area was measured using the Brunauere Emmette Teller (BET) method (Micromeritics analyzer ASAP 2020 (USA)) at liquid nitrogen temperature. Raman spectra were collected with Renishaw INVIA Raman System (532 nm). Angle-dependent X-ray photoelectron spectroscopy (XPS) analysis was performed on a KRATOS XSAM 800 X-ray photoelectron spectrometer.

2.3. Electrochemical measurements

To prepare electrodes for a supercapacitor, 3D graphene, acetylene black and sodium carboxymethylcellulose (CMC) with a weightratio of 8:1:1 were adequately mixed with water and pasted on a copper foil to form a very homogeneous film, after dried at 80 °C for 6 h in vacuum oven, it was compressed to obtain round electrodes (average thickness ≈ 200 μm). Two pieces of the same weight electrodes were then pressed together to make a double-layer supercapacitor device, the MPF30AC nonwoven separator (purchased from NKK) was used as diaphragm, and the 6 M KOH solution was used as the electrolyte. All cyclic voltammetry (CV) and galvanostatic charge/discharge were performed on a CHI 660D workstation.

3. Results and discussion

The 3D honeycomb-like nitrogen-doped graphene was designed on the basis of the following two considerations. First, planar Pc molecules intercalate between GO layers by self-assembly (Fig. 1(a) and (b)). Second, the interlaminated Pc molecules pyrolyze into small carbon molecules and conjugate with the graphene framework at 800 °C (Fig. 1(c) and (d)). The synthesized 3D honeycomb-like graphene contains (i) abundant meso- and macropores that provide a high surface area of ~230 m^2 g^{-1}, resulting in large capacitance; (ii) interconnected meso-, and macropores that act as ion channels to facilitate ion transportation; (iii) nitrogen atoms doped into the 3D graphene framework in a simple one-step process to enhance capacitance.

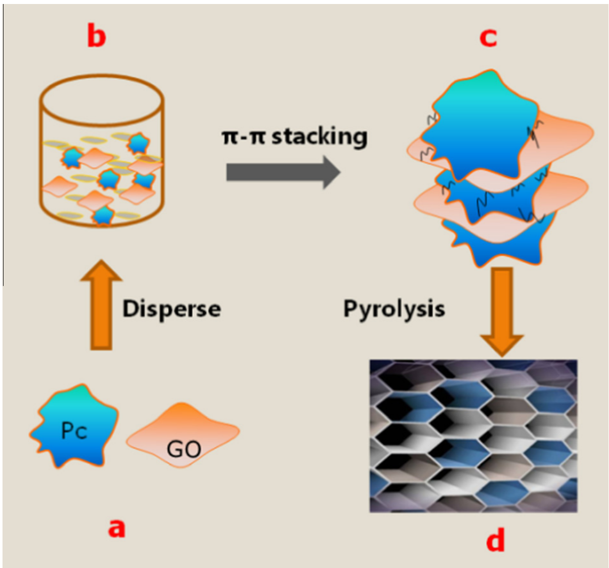

Fig. 1. Fabrication process of 3D graphene. (a) Metal-free phthalocyanine (Pc) and graphene oxide (GO); (b) Pc and GO are dispersed in a vessel; (c) PC and GO self-assemble through π–π stacking interactions during stirring; (d) ideal structure model of 3D graphene.

Scanning Electron Microscopy (SEM) was conducted to view the microstructure of 2D graphene (Fig. 2(a)), Pc carbon (Fig. 2(b)), and the 3D graphene (Fig. 2(c)–(f)). The unique interconnected honeycomb-like network of 3D graphene is observed in Fig. 2(c)–(f). The magnified SEM images (Fig. 2(c) and (d)) clearly show an interconnected network of submicrometer-sized macropores in the 3D graphene. The interconnected 3D network was further confirmed by transmission electron microscopy (TEM); a continuous 3D porous network was observed (Fig. 2(g)). The selected-area electron diffraction (SAED) pattern of the 3D graphene in Fig. 2 (h) displays the typical hexagonal crystalline structure of graphene. In contrast, the 2D graphene and Pc carbon sintered from the GO and Pc molecules possessed a stacked layer structure.

The nitrogen adsorption-desorption isotherm of the 3D graphene (Fig. 3) exhibits the characteristics of a type-V isotherm with a Brunauer–Emmett–Teller surface area of 229.7 m^2 g^{-1}. The 3D graphene contains a porous network with pore widths ranging from 25 to 300 nm, which is clearly visible in the SEM images showing the edges of multilayer graphene (see Fig. 2(c) and (d)). From the microstructure analysis, we believe that Pc, a 2D planar aromatic macrocycle, is able to self-assemble into the GO layer through π–π intermolecular interactions. The metal-free phthalocyanines are porphyrin derivatives with a high electronic delocalization. The two common bonding configurations, quaternary nitrogen and pyridinic nitrogen, are sp^2 hybridized within the carbon bond, and the mass percent of eight nitrogen atoms in the molecule is above 21 wt%. During the procedure, planar phthalocyanine (Pc) molecules as building blocks intercalate through self-assembly between graphene oxide (GO) layers *via* hydrogen bonding and π–π stacking interactions. Therefore, the GO sheets can be regarded as 2D conjugated multilayer complex architecture macromolecules with extremely large molar mass based on their